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(11) **EP 0 386 720 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
26.06.1996 Bulletin 1996/26

(51) Int Cl.⁶: **C08L 29/04**, C08L 23/08,
C08K 13/02, B32B 27/30,
B32B 27/32

(21) Application number: **90104334.9**

(22) Date of filing: **07.03.1990**

(54) **Composition, multilayered container and package**

Zusammensetzung, mehrschichtiger Behälter und Verpackung

Composition, récipient multicouche et emballage

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **08.03.1989 JP 57581/89**

(43) Date of publication of application:
12.09.1990 Bulletin 1990/37

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- **PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 11, no. 371, December 3, 1987 THE PATENT OFFICE JAPANESE GOVERNMENT page 60 C 462**

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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Description

The present invention relates to compositions which generate little odorous components and are excellent in thermal stability, to multilayered containers which can pack and contain various foods, in particular various liquid foods and beverages, e.g. straight juices of citrus fruits, such as orange juice and lemon juice, as well as cosmetics and perfumes, without impairing their good flavor and/or good odor, and further to packages, particularly food packages, comprising such containers containing various contents, with high quality and excellent keeping property.

Recently, as containers e.g. for liquid foods, besides conventional glass bottles and metal cans, multilayered structures comprising thermoplastic resins and composite containers comprising paper and thermoplastic resin layers have been widely used.

The above containers, however, cause problems of deterioration of the contents, especially of foods. Particularly, when the contents are juices of citrus fruits or foods containing such fruits, terpene hydrocarbons such as d-limonene which constitute the flavor component tend to be absorbed in polyolefins such as polyethylene, which are widely used for the innermost layer of such containers. The reduction of the flavor components of a food during its storage necessarily leads to deterioration of the flavor, thereby minimizing its commercial value.

With saponified products of an ethylene-vinyl acetate copolymer (hereinafter referred to as EVOH) being used instead of polyolefin resins for the innermost layer, the absorption of the flavor components is, as described in JP-A-3950/1988, markedly reduced and the flavor does hence not deteriorate so much. However, conventional EVOH has still the following problem. Containers comprising conventional EVOH often produce an irritating odor due to isolation of residual acetic acid, or produce acetaldehyde, crotonaldehyde, aldol or the like as its pyrolysate, so that the containers cannot exhibit a sufficient preservability for food flavors. Even when the contents are good-smelling cosmetics or perfumes, which are non-foods, their odors deteriorate from the same reason, which is not preferred.

JP-A-62-143954 discloses an EVOH which provides molded articles free from fish eye and which has improved heat stability in melt molding.

The copolymer contains 20-60 mol % ethylene and has a saponification degree of ≥ 90 mol % of the vinyl acetate.

It is treated with an acid like acetic acid or ortho phosphoric acid and a calcium primary salt or a magnesium salt of a polybasic acid. The EVOH has an alkali metal content of 0.001-0.025 weight %, a ratio of alkali metal/phosphate ions of 0.1-5, and a ratio of Ca or Mg/phosphate ions of 0.3-1.3.

However, the EVOH does not have sufficient thermal stability because of the use of the specific metal phosphates and further is not given consideration for suppressing generation of odorous components at all. JP-A-955/1977 and 49294/1976 disclose the incorporation of metal salts and acetic acid into EVOH for the purpose of providing the EVOH with thermal stability. These former two have not been able to succeed in suppressing generation of odorous components because of large incorporation of acetic acid. Furthermore, none of the above literature describes the provision of the EVOH composition at the innermost layer of a multilayered container.

Accordingly, an object of the present invention is to provide EVOH compositions without the above-mentioned problems, by the use of which the flavor components of liquid foods such as citrus fruit juices, the components for desirable high-quality odors of cosmetics and perfumes, are not absorbed in the container and, at the same time, odorous components deteriorating the flavor of the contained foods or the good odor of e.g. the contained cosmetics are not generated from the inner surface of the container body.

Another object of the present invention is to provide multilayered containers comprising such compositions as the innermost layer.

Still another object of the present invention is to provide packages comprising such containers and their contents, having high quality and excellent storing capability.

The above objects are solved by the following specific EVOH compositions which generate little odorous components and at the same time have excellent thermal stability. The composition comprises a saponified product of an ethylene-vinyl acetate copolymer having an ethylene content of 20 to 80 mol% and a saponification degree of the vinyl acetate component of at least 95 mol%, said compositions containing 20 to 200 ppm as converted to alkali metal of an alkali metal acetate, not more than 10 ppm of metals belonging to the group II of the periodic table, 30 to 250 ppm of acetic acid, and 5 to 500 ppm as converted to phosphate ion of phosphoric acid or an alkali metal hydrogenphosphate, and having a content ratio of acetic acid/alkali metal acetate of from 0.1 to 1 and the flow characteristic that the extrusion rate with a capillary rheometer (Koka Flow Tester) at at least one temperature from 10° to 80°C above the melting point does not increase to an extent that V_{10}/V_0 is more than 1.1, V_0 and V_{10} being the extrusion rate at the beginning and 10 hours after the beginning of heating, respectively.

Additionally the afore-mentioned problems can be solved by multilayered containers comprising a layer of a composition according to the present invention as the innermost layer.

The compositions, in particular EVOH compositions used for the innermost layer of multilayered containers must be ones specified above.

The alkali metal acetate herein is sodium acetate, potassium acetate or lithium acetate, the former two being

preferred. It is necessary that the content of the alkali metal acetate be from 20 to 200 ppm as converted to the alkali metal. If the content is less than 20 ppm, the EVOHs will not give a multilayered structure with neat appearance due to coloring and formation of many gelled matters perhaps because such EVOHs readily oxidize upon melt formation. On the other hand, if the content exceeds 200 ppm, the EVOHs will readily decompose thermally at the molding of multilayered containers, thereby generating odorous compounds such as acetaldehyde, crotonaldehyde and aldol, which then migrate into the contents such as foods, which is not preferred. The content of the alkali metal salts is more preferably in the range of from 40 to 150 ppm.

The metals belonging to the group II of the periodic table should not necessarily be incorporated. If they be ever incorporated, the content is preferably not more than 10 ppm. Since the metals have markedly larger properties to pyrolyze EVOH than alkali metal acetate, a content of such metals exceeding 10 ppm will cause to generate large amounts of the above-mentioned odorous materials, which is not preferred. The metals belonging to group II of the periodic table herein are calcium, magnesium, beryllium, zinc and barium, and they are contained in EVOH in the form of compounds such as carbonate and acetate.

It is necessary that the content of acetic acid be 30 to 250 ppm. If the content is less than 30 ppm, the effect of the acetic acid to prevent alkali metal acetates or the metals belonging to group II of the periodic table from pyrolyzing EVOH will not fully exhibit, thereby causing the above-mentioned odorous components to generate. On the other hand, if the content exceeds 250 ppm, the acetic acid will migrate from the innermost layer, i.e. the EVOH layer, of the multilayered container into the contents and smell irritatingly. The content of acetic acid is more preferably in the range of from 40 to 240 ppm.

It is necessary that the content of the phosphoric acid or alkali metal hydrogenphosphates be from 5 to 500 ppm as converted to phosphate ion. Examples of the alkali metal hydrogenphosphate are disodium hydrogenphosphate, sodium dihydrogenphosphate, dipotassium hydrogenphosphate and potassium dihydrogenphosphate, among which sodium dihydrogenphosphate and potassium dihydrogenphosphate are preferably used. If the content of phosphate ion is less than 5 ppm, their effect of preventing alkali metal acetates or the metals belonging to group II of the periodic table from pyrolyzing EVOH will not fully exhibit, thereby causing the above-mentioned odorous components to generate. On the other hand, if the content exceeds 500 ppm, the phosphate ions will generate a special odor resulting perhaps from their pyrolysis. The content of phosphate ion is more preferably in the range of from 10 to 350 ppm.

It is necessary that the content ratio of acetic acid to alkali metal acetates be from 0.1 to 1. If the ratio is less than 0.1, the EVOHs will generate a strong pyrolysis odor even when the contents of acetic acid, alkali metal acetates and phosphate ion are all within the appropriate ranges, i.e. 30 to 250 ppm, 20 to 200 ppm as converted to alkali metals and 5 to 500 ppm, respectively. On the other hand if the ratio exceeds 1, the EVOHs will not give a multilayered structure with neat appearance due to coloring and formation of many gelled matters perhaps because such EVOHs readily oxidize upon melt formation. The ratio is more preferably in the range of from 0.2 to 0.9.

It is preferred that the content ratio of phosphoric acid or alkali metal hydrogenphosphates to alkali metal acetates be in the range of from 0.02 to 10 and more preferably in the range of from 0.03 to 5.

Here, the contents of the above-mentioned components refer to the EVOH composition before molding and not to the innermost layer after the molding. The abovementioned contents are all based on weight, and measured according to the following methods.

① Alkali metal acetates

Place 100 parts of a EVOH composition in 250 parts of a 0.1N aqueous nitric acid solution. Heat the mixture while stirring at a mature of 95°C for 3 hours, and then filter the mixture. Determine the concentration of alkali metals in the filtrate by ion chromatography. Since all the alkali metals of the EVOH composition has been extracted into the aqueous nitric acid solution during the above heating, the concentration of the alkali metals in the filtrate thus determined gives by calculation the content of the alkali metals in the EVOH composition. Determine the amount of acetate ion of the alkali metal acetates as follows. First determine the total amount of acetate ions, X, from the alkali metal acetates and from acetic acid by ion chromatography. The amount of acetate ion, Y, of acetic acid is determined by method ③. Subtract Y from X to obtain the amount of the acetate ions of the alkali metal acetates.

② Metals belonging to group II of the periodic table

The content of these metals is determined in the same manner as for alkali metal acetates.

③ Acetic acid

Place 100 parts of a EVOH composition in 250 parts of deionized water. Heat the mixture while stirring at a temperature of 95°C for 3 hours, and then filter the mixture. Titrate the acetic acid in the filtrate with sodium hydroxide.

Since all the acetic acid of the EVOH composition has been extracted into the deionized water during the above heating, the concentration of the acetic acid in the filtrate thus determined gives by calculation the content of the acetic acid in the EVOH composition.

5 ④ Phosphoric acid and alkali metal hydrogenphosphates

Determine the amount of phosphate ions and alkali metals in the same manner as in ①.

Besides the above, the EVOH compositions according to the present invention must have the flow characteristic that the extrusion rate does not substantially increase for at least 10 hours in the relationship between the heating time and the extrusion rate with a capillary rheometer (Koka Flow Tester) at at least one temperature from 10 to 80°C above the melting point. In the case of an EVOH composition with which the extrusion rate starts increasing within 10 hours, the EVOHs will tend to generate an intense pyrolysis odor when its melt formation is performed continuously over a long time period. The extrusion rate with Koka Flow Tester herein means the amount extruded per unit time under a load of 10 kg/cm² through a nozzle having an inner diameter of 1 mm and a length of 10 mm. The expression "does not substantially increase" herein means that, with V_0 and V_{10} being the extrusion rate at the beginning (heating time: 0) and that 10 hours after the start of the heating respectively, V_{10}/V_0 is not more than 1.1, preferably not more than 1.05. V_{10}/V_0 is preferably at least 0.05, more preferably at least 0.1.

In the present invention, it is necessary that the ethylene content and the saponification degree of the vinyl acetate component of EVOHs be 20 to 80 mol% and at least 95 mol%, respectively.

20 If the ethylene content is less than 20 mol%, the EVOHs will readily gel, thereby rendering their melt formation operation difficult to conduct over a long time period. On the other hand, if the ethylene content exceeds 80 mol%, the EVOHs will absorb flavor components such as d-limonene to a large extent, thereby deteriorating the taste of the contents. For the purpose of providing high oxygen barrier properties while minimizing the absorption of flavor components, the ethylene content is preferably 25 to 70 mol%, more preferably 25 to 60 mol%.

25 If the saponification degree is less than 95 mol%, the EVOHs will again readily gel and, like the case of low ethylene content, a long-period melt formation operation is difficult to achieve. More preferably, the saponification degree is at least 98 mol%.

While there is no specific restriction as to the melt index (210°C, 2160 g) of the EVOHs, it is preferably in the range of from 0.2 to 120 g/10 min, more preferably in the range of from 1.0 to 60 g/10 min.

30 The EVOH compositions of the present invention may be modified with not more than 5 mol% of copolymerizable monomers. Examples of copolymerizable monomers are propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, acrylic acid esters, methacrylic acid esters, maleic acid, fumaric acid, itaconic acid, higher fatty acid vinyl esters, alkyl vinyl ethers, N-vinylpyrrolidone, N-n-butoxymethylacrylamide, vinyltrimethoxysilane, vinylmethyldimethoxysilane, vinylidimethylmethoxysilane, N-(2-dimethylaminoethyl)methacrylamide and quaternary compounds thereof; N-vinylimidazole and quaternary compound thereof.

35 The EVOH compositions, particularly those used for the innermost layer of multilayered containers, according to the present invention are produced by for example the following process. Ethylene and vinyl acetate are copolymerized with a known radical polymerization initiator such as α, α' -azobis-iso-butyronitrile in the presence or absence of an alcohol such as methanol to give an ethylene-vinyl acetate copolymer. The obtained ethylene-vinyl acetate copolymer is then saponified in the presence of an alkali catalyst such as sodium hydroxide or potassium hydroxide. The saponified product, i.e. EVOH, is washed e.g. with deionized water which contains little metal ions, chloride ion and the like to remove sodium acetate, potassium acetate or the like which has been formed by the saponification reaction. Here, part of the sodium acetate, potassium acetate or the like may remain unremoved. Next, the EVOH is mixed with the prescribed amounts of acetic acid, an alkali metal acetate such as sodium acetate and a compound containing phosphate ions such as sodium dihydrogenphosphate, and the mixture is dried. Here, these substances may directly be added to the EVOH, or be first dissolved in deionized water which contains few ions, followed by immersion of the EVOH in the thus obtained solution.

40 Now the multilayered containers comprising the EVOH composition of the present invention as their innermost layer are described below. Examples of the layer construction of the multilayered containers are:

- 50
- (1) 2 layers: C/A
 - (2) 3 layers: C/B/A, C/B/(A+B), C/B/(A+B+C)
 - (3) 4 layers: C/B/(A+B+C)/A, C/B/A/(A+B+C)
 - (4) 5 layers: C/B/A/B/C, C/B/(A+B+C)/B/C
 - 55 (5) 6 layers: C/B/A/(A+B+C)/B/A, C/B/A/C/B/A
 - (6) 7 layers: C/B/A/B/C/B/A, C/B/(A+B+C)/B/C/B/A

and the like wherein A means a layer of a thermoplastic resin with low water absorbability provided outside the EVOH

composition layer, C, and B means an adhesive layer. Further examples with paper being provided outside the EVOH composition layer are: C/A/paper/A, C/A/paper/(A+C) and C/B/A/paper/A. Other constructions are also applicable and an aluminum layer may also be provided.

In the above constructions, while the layer C (EVOH composition layer) must constitute the innermost layer, it may also constitute, additionally, other layers, which will provide containers having still higher keeping properties. The innermost layer herein means a layer which directly contact the contents when a liquid article or paste article is packed.

Examples of the thermoplastic resins with low water absorbability are polyolefins such as polyethylene (low density, medium density or high density), polypropylene and ethylene-propylene copolymers, ethylene-vinyl acetate copolymers, thermoplastic polyesters, polyamides, polystyrene, polycarbonates, polyvinyl chloride, acrylic resins such as polyacrylonitrile, polyacetals and their mixtures; among which particularly preferred are polyethylene, polypropylene, ethylene-propylene copolymers and their mixtures.

Various adhesive resins can be used for the adhesive layers, B, and they are selected depending on the kind of the resin to be bonded to the EVOH composition layers. Representative adhesives which provide particularly firm bond to the EVOH compositions of the present invention are carboxyl-containing modified olefin polymers obtained by chemically bonding (e.g. by addition or grafting) unsaturated carboxylic acids or their anhydrides to olefin polymers, e.g. polyolefins such as low-density polyethylene, high-density polyethylene, linear low-density polyethylene, polypropylene and polybutene, copolymers of olefins with a comonomer copolymerizable with the olefins (for example, vinyl esters, unsaturated carboxylic acid esters) such as ethylene-vinyl acetate copolymers and ethylene-ethyl ester copolymers. Preferred examples of such carboxyl-containing modified olefins are polyethylenes modified by grafting of maleic anhydride, polypropylenes modified by grafting of maleic anhydride, ethylene-ethyl acrylate copolymers modified by grafting of maleic anhydride, ethylene-vinyl acetate copolymers modified by grafting of maleic anhydride and their mixtures. These adhesive resins may be blended with an EVOH, for example with the afore-mentioned EVOH compositions.

In the present invention, the above-mentioned layer C (EVOH composition layer) may optionally incorporate or, sometimes, preferably incorporate the above-mentioned thermoplastic resins(A) with low water absorbability and/or adhesive resins (B). For example, with the containers of the present invention being to be boil sterilized or retort sterilized, the innermost layer (C) can be prevented from being mal-formed by incorporating therein of at least one polyolefin, thermoplastic polyester, polyamide or polycarbonate. The incorporation ratio based on the total weight of the EVOH composition (C) and the thermoplastic resin (A) having low water absorbability being preferably at least 3 wt%, more preferably at least 5 wt%, most preferably at least 15 wt% and preferably not more than 97 wt%, more preferably not more than 45 wt%, most preferably not more than 35 wt%.

According to the present invention, parisons, sheets or films having the above multilayered construction are formed by coextrusion, lamination or similar processes and the parisons, sheets or films thus formed are then formed e.g. into bottles, cups, pouches, tubes by known processes.

Formation processes for typical multilayered containers are now described more concretely.

Preparation of bottles is first described, since in the present invention particularly significant effect is produced when the multilayered container is a bottle.

Bottles are produced by a process which comprises obtaining multilayered hot parisons by coextrusion and then directly blowing the hot parisons into bottles, or a process which comprises obtaining multilayered cold parisons (parisons with a bottom, pipes) by coextrusion or coinjection and then biaxially stretch-blowing the cold parisons into bottles. With the direct blow molding being used, hot parisons are partly bitten off by the pinch-off of the mold used in the blow molding, whereby two portions of the EVOH in the innermost layer join with each other and, at the same time, the adhesive layer neighboring the EVOH layer becomes thin at the pinch-off part, of all the bottles formed. As a result, with conventional EVOH being used, the adhesiveness to the adhesive layer often becomes low and the pinch-off part will hence often be of very low strength. On the contrary, bottles using the EVOH compositions of the present invention not only prevent odorous components from generating, but have sufficient strength for the practical purpose even at their pinch-off part.

Preparation of cups is next described. Sheetings of the above-described resin layers are formed e.g. by a T-die process or tubular film formation. The sheetings are then formed by plug-assist molding, drawing by using die and punch, pressure formation, drawing with ironing processes into non-joint, cup-shaped multilayered drawn containers having for example the afore-mentioned C/B/A/C/B/A construction with the layer C (EVOH layer) at least as the innermost layer.

Lastly, preparation of multilayered containers comprising a paper layer is described with an example of the above-mentioned C/A/paper/A construction. Both sides of a paperboard are flame treated, and then for example a low-density polyethylene layer each is extrusion-laminated on each side to form layer A. Next, the surface of the layer A (low-density polyethylene layer) of the layer-C side is corona discharged, followed by extrusion lamination or dry lamination thereon of the EVOH layer to form the layer C. The multilayered structure thus formed is molded, with the layer C being the innermost layer, into containers having e.g. a rectangular or parallelepiped shape.

The multilayered containers of the present invention are useful for various beverages and liquid foods, examples

being:

Fruit juices

- 5 Straight juices: orange juice, lemon juices, plum juice, grape juice, strawberry juice
 Processed fruit juices: nectar

Green juices: vegetable juices, tomato juice

Synthetic beverages

- 10 Those containing synthetic fruit juices utilizing citric acid, colorants, perfumes, saccharides such as sugar and fructose, and vitamins as required.

Lactic acid beverages

Cooked curry

Stews: stewed beef

- 15 Soups: consomme, potage, miso-soup

Refreshments: "Zenzai" (thick bean-meal soup with sugar and rice cake), boiled adzuki-bean, "Shiruko" (adzuki-bean soup with sugar and rice cake), "Anmitsu" (boiled peas with honey and bean-jam), "Mitsu-mame" (boiled beans, agar-agar cubes and other delicacies with treacle poured on), jelly

Processed sea foods and livestock products bacon, boiled fish paste, hamburgers, sausage, ham

- 20 Fruits: orange, pineapple, cherry

Condiments: soybean sauce, sauce, vinegar, dressings, catsups, mayonnaise, edible oil, miso

Bread auxiliaries: margarine, butter, jam

Alcoholic beverages: beer, sake, whisky, wines, cocktails such as gin fizz.

- 25 Furthermore, the containers of the present invention can be suitably used for containing medicines such as Ringer's solution, agricultural chemicals, cosmetics and washing agents.

The containers of the present invention are particularly suitable for, among the above-mentioned items, containing citrus fruit juices or carbonated water containing them.

- 30 Packages of liquid foods, cosmetics or perfumes contained in the containers of the present invention are very valuable, since they have high qualities and good storage capability.

Other features of the invention will become apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof. In the Examples, "parts" and "%" are based on weight unless otherwise specified.

35 Example 1

- Methanol vapor was blown into a solution comprising 45 parts of an ethylene-vinyl acetate copolymer having an ethylene content of 28 mol%, 50 parts of methanol and 1 part of sodium hydroxide at 110°C and under a pressure of 3.5 kg/cm²G for 40 minutes to effect saponification reaction, while methyl acetate generating during the reaction was
 40 distilled off with part of methanol and removed from the system. The thus obtained reaction mixture (saponification degree of vinyl acetate component: 99.3 mol%) was extruded through a die having a diameter of 2 mm into a solution of industrial water/methanol (weight ratio: 90/10) to be coagulated therein into a strand, which was then cut with a cutter to pellets. The industrial water used contained 9.4 ppm of calcium ions and 1.2 ppm of magnesium ions. One part of the pellets was washed 3 times with an aqueous solution containing 0.01 part of acetic acid dissolved in 100
 45 parts deionized water. Next, the washed pellets were immersed for 3 hours in an aqueous solution of 0.03 part acetic acid, 0.02 part potassium acetate and 0.005 part sodium dihydrogenphosphate dissolved in 100 parts deionized water, squeezed and then dried. The EVOH pellets after being dried contained 140 ppm of potassium acetate as converted to potassium, 150 ppm of acetic acid, 45 ppm of sodium dihydrogenphosphate as converted to phosphoate ion, 3 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH
 50 showed a content ratio of acetic acid/potassium acetate of 0.4, and had a moisture content of 0.1%, MI (210°C, 2160 g) of 3.5 g/10 min and a melting point of 190°C. The extrusion rate of the EVOH through a Koka Flow Tester (type 301, made by Shimazu Corporation) at 220°C did not substantially increase over more than 10 hours ($V_{10}/V_0 = 0.10$). The extrusion rate with Koka Flow Tester herein means the amount extruded per unit time under a load of 10 kg/cm² through a nozzle having an inner diameter of 1 mm and a length of 10 mm.

- 55 The EVOH composition thus obtained was used for the formation of bottles having a construction of EVOH/adhesive resin/EVOH/adhesive resin/high-density polyethylene, in which the EVOH was provided as the innermost layer and as the intermediate layer, through a 3 kind/5 layer direct blow molding machine at a die temperature of 240°C. As the adhesive resin, a maleic anhydride-modified ethylene-vinyl acetate copolymer having an MI (190°C, 2160 g) of 1.8

g/10 min, a maleic anhydride content of 0.5% and vinyl acetate content of 20% are used. The high-density polyethylene used was one having an MI (190°C, 2160 g) of 1.0 g/10 min and a density of 0.945 g/cm³. Thus prepared were bottles of 2-liter capacity fitted with a handle and having a thickness (body) of the layers of 45/21/30/21/280 in μm in the order listed above.

The bottles were each aseptically filled with 1.8ℓ of a condensed reduced 100% orange juice, and the packages were stored at 5°C for 8 weeks. After the storage, the orange juice contained was tested for the content of d-limonene and by organoleptic test for flavor and taste by 5 panelists. The results are shown in Table 1. The content of d-limonene was determined by head-space gas chromatography. The ratings for flavor and taste were, based on those of fresh orange juice, as follows:

- A: same as the flavor or taste of fresh orange juice
- B: a little different from the flavor or taste of fresh orange juice but not unpleasant.
- C: different from the flavor or taste of fresh orange juice and unpleasant.

For the purpose of testing the bottle strength, 20 bottles containing orange juice were dropped from the height of 2 m, but none of them were broken.

Example 2

Procedures similar to those described in Example 1 were followed to prepare an EVOH composition containing acetic acid, sodium acetate and phosphoric acid and an EVOH having an ethylene content of 38 mol%, saponification degree of 99.5 mol%, an MI (210°C, 2160 g) of 3.3 g/10 min and a melting point of 176°C. The EVOH composition obtained contained 100 ppm of sodium acetate as converted to sodium, 230 ppm of acetic acid, 15 ppm of phosphoric acid as converted to phosphate ion, 5 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH composition showed a content ratio of acetic acid/sodium acetate of 0.65, and had a moisture content of 0.1%. The extrusion rate of the EVOH composition through a Koka-type flow tester at a temperature of 220°C did not substantially increase over more than 10 hours ($V_{10}/V_0 = 0.33$).

The EVOH pellets obtained were formed into bottles in the same manner as in Example 1, and the bottles were subjected to the test for storing capability with orange juice. The results are also shown in Table 1. The bottles were also tested for strength by the dropping test in the same manner as in Example 1 and none of them were broken.

Example 3

Procedures similar to those described in Example 1 were followed to prepare an EVOH composition containing acetic acid, sodium acetate and potassium dihydrogenphosphate and an EVOH having an ethylene content of 44 mol%, saponification degree of 99.1 mol%, an MI (210°C, 2160 g) of 8.2 g/10 min and a melting point of 163°C. The EVOH composition obtained contained 50 ppm of sodium acetate as converted to sodium, 50 ppm of acetic acid, 300 ppm of potassium dihydrogenphosphate as converted to phosphate ion, 5 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH composition showed a content ratio of acetic acid/sodium acetate of 0.28, and had a moisture content of 0.22%. The extrusion rate of the EVOH through a Koka Flow Tester at a temperature of 220°C did not substantially increase over more than 10 hours ($V_{10}/V_0 = 0.42$).

The EVOH pellets were formed into bottles in the same manner as in Example 1, and the bottles were tested for storing capability with orange juice. The results are also shown in Table 1. The bottles were also tested for strength by the dropping test in the same manner as in Example 1 and none of them were broken.

Example 4

Procedures similar to those described in Example 1 were followed to prepare an EVOH composition containing acetic acid, sodium acetate and sodium dihydrogenphosphate and an EVOH having an ethylene content of 55 mol%, a vinyltrimethoxysilane content of 0.015 mol%, a saponification degree of 98.4 mol%, an MI (210°C, 2160 g) of 9.4 g/10 min and a melting point of 145°C. The EVOH composition obtained contained 80 ppm of sodium acetate as converted to sodium, 70 ppm of acetic acid, 30 ppm of sodium dihydrogenphosphate as converted to phosphate ion, 3 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH composition showed a content ratio of acetic acid/sodium acetate of 0.25, and had a moisture content of 0.11%. The extrusion rate of the EVOH through a Koka Flow Tester at a temperature of 200°C did not substantially increase over more than 10 hours ($V_{10}/V_0 = 0.54$).

The EVOH pellets were formed into bottles in the same manner as in Example 1, and the bottles were tested for storing capability with orange juice. The results are also shown in Table 1. The bottles were also tested for strength by

the dropping test in the same manner as in Example 1 and none of them were broken.

Comparative Example 1

Bottles were formed in the same manner as in Example 1 except for using as the innermost layer high-density polyethylene instead of the EVOH composition described in Example 1. The bottles had a construction of (inner) high-density polyethylene/adhesive resin/EVOH/adhesive resin/high-density polyethylene (outer) with the thicknesses being 50/21/45/21/280 (μm). The bottles were tested for storing capability with orange juice. The results are also shown in Table 1. The content of d-limonene markedly decreased and the taste worsened to a great extent.

Comparative Example 2

Procedures similar to those described in Example 1 were followed to prepare an EVOH composition containing acetic acid, sodium acetate and calcium hydrogenphosphate and an EVOH having an ethylene content of 38 mol%, a saponification degree of 99.5 mol%, an MI (210°C, 2160 g) of 3.4 g/10 min and a melting point of 176°C. The EVOH composition obtained contained 110 ppm of sodium acetate as converted to sodium, 50 ppm of acetic acid, 70 ppm of calcium hydrogenphosphate as converted to phosphate ion, 20 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH composition showed a content ratio of acetic acid/sodium acetate of 0.13, and had a moisture content of 0.1%. The extrusion rate of the EVOH through a Koka Flow Tester at a temperature of 220°C first decreased with time for 5 hours, then gradually increased and 8 hours after the start became 4 times as high as at the start.

The EVOH pellets were formed into bottles in the same manner as in Example 1, and the bottles were tested for storing capability with orange juice. The results are also shown in Table 1. The bottles generated, just after being formed, an intense burning odor which was thought to come from pyrolysis of the EVOH. The test of the gas contained in the bottle indicated the presence of e.g. acetaldehyde, crotonaldehyde and aldol, which were not observed in Examples 1 through 4.

Comparative Example 3

Procedures similar to those described in Example 1 were followed to prepare an EVOH composition containing acetic acid, sodium acetate and potassium dihydrogenphosphate and an EVOH having an ethylene content of 38 mol%, a saponification degree of 99.5 mol%, an MI (210°C, 2160 g) of 3.4 g/10 min and a melting point of 176°C. The EVOH composition obtained contained 150 ppm of sodium acetate as converted to sodium, 40 ppm of acetic acid, 70 ppm of potassium dihydrogenphosphate as converted to phosphate ion, 8 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH composition showed a content ratio of acetic acid/sodium acetate of 0.07, and had a moisture content of 0.1%. The extrusion rate of the EVOH through a Koka Flow Tester at a temperature of 220°C first decreased with time for 8 hours, but then after 10 hours after the start increased up to 1.9 times the value at the start ($V_{10}/V_0 = 1.9$).

The EVOH pellets were formed into bottles in the same manner as in Example 1, and the bottles were tested for storing capability with orange juice. The results are also shown in Table 1. The bottles generated, just after being formed, an intense burning odor which was thought to come from pyrolysis of the EVOH. The test of the gas contained in the bottle indicated, same as in Comparative Example 2, the presence of e.g. acetaldehyde, crotonaldehyde and aldol.

Comparative Example 4

Procedures similar to those described in Example 1 were followed to prepare an EVOH composition containing acetic acid, sodium acetate and potassium dihydrogenphosphate and an EVOH having an ethylene content of 38 mol%, a saponification degree of 99.5 mol%, an MI (210°C, 2160 g) of 3.3 g/10 min and a melting point of 176°C. The EVOH composition obtained contained 50 ppm of sodium acetate as converted to sodium, 350 ppm of acetic acid, 15 ppm of potassium dihydrogenphosphate as converted to phosphate ion, 5 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH composition showed a content ratio of acetic acid/sodium acetate of 2.0 and had a moisture content of 0.15%. The extrusion rate of the EVOH through a Koka Flow Tester at a temperature of 220°C did not substantially increased over 10 hours ($V_{10}/V_0 = 0.27$).

The EVOH pellets were formed into bottles in the same manner as in Example 1, and the bottles were tested for storing capability with orange juice. The results are also shown in Table 1. The bottles generated, just after being formed, an intense acetic acid odor.

Comparative Example 5

Procedures similar to those described in Example 1 were followed to prepare an EVOH composition containing acetic acid, sodium acetate and potassium dihydrogenphosphate and an EVOH having an ethylene content of 44 mol%, a saponification degree of 99.1 mol%, an MI (210°C, 2160 g) of 8.1 g/10 min and a melting point of 163°C. The EVOH composition obtained contained 60 ppm of sodium acetate as converted to sodium, 100 ppm of acetic acid, 550 ppm of potassium dihydrogenphosphate as converted to phosphate ion, 8 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH composition showed a content ratio of acetic acid/sodium acetate of 0.47, and had a moisture content of 0.1%. The extrusion rate of the EVOH through a Koka Flow Tester at a temperature of 200°C did not substantially increase over 10 hours ($V_{10}/V_0 = 0.41$).

The EVOH pellets were formed into bottles in the same manner as in Example 1, and the bottles were tested for storing capability with orange juice. The results are also shown in Table 1. The bottles generated, just after being formed, an intense peculiar odor.

Comparative Example 6

Example 1 was repeated except for changing the amount of sodium hydroxide to 0.7 to prepare an EVOH composition. The EVOH composition had a saponification degree of 94.3 mol%, and contained 140 ppm of potassium acetate as converted to potassium, 150 ppm of acetic acid, 45 ppm of potassium dihydrogenphosphate as converted to phosphate ion, 8 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH composition showed a content ratio of acetic acid/sodium acetate of 0.57, and had a moisture content of 0.15%. The EVOH composition had an MI (210°C, 2160 g) of 3.7 g/10 min and a melting point of 190°C. The extrusion rate of the EVOH through a Koka Flow Tester at a temperature of 220°C did not substantially increased over 10 hours ($V_{10}/V_0 = 0.02$).

An attempt was made to form the thus obtained EVOH composition into bottles in the same manner as in Example 1, but bottles with neat appearance and high commercial value could not be obtained because the EVOH readily gelled.

Comparative Example 7

Procedures similar to those described in Example 1 were followed to prepare an EVOH composition containing acetic acid, sodium acetate and potassium dihydrogenphosphate and an EVOH having an ethylene content of 18 mol%, a saponification degree of 99.8 mol%, an MI (230°C, 2160 g) of 6.2 g/10 min and a melting point of 205°C. The EVOH composition obtained contained 120 ppm of sodium acetate as converted to sodium, 110 ppm of acetic acid, 80 ppm of potassium dihydrogenphosphate as converted to phosphate ion, 4 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH composition showed a content ratio of acetic acid/sodium acetate of 0.26, and had a moisture content of 0.13%. The extrusion rate of the EVOH composition through a Koka Flow Tester at a temperature of 230°C did not substantially increased over 10 hours ($V_{10}/V_0 = 0.01$).

An attempt was made to form the thus obtained EVOH composition into bottles in the same manner as in Example 1, but bottles with neat appearance and high commercial value could not, like in Comparative Example 6, be obtained because the EVOH readily gelled.

Comparative Example 8

Procedures similar to those described in Example 1 were followed to prepare an EVOH composition containing acetic acid, sodium acetate and potassium dihydrogenphosphate and an EVOH having an ethylene content of 38 mol%, a saponification degree of 99.5 mol%, an MI (210°C 2160 g) of 3.3 g/10 min and a melting point of 176°C. The EVOH composition obtained contained 10 ppm of sodium acetate as converted to sodium, 35 ppm of acetic acid, 20 ppm of potassium dihydrogenphosphate as converted to phosphate ion, 5 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH composition showed a content ratio of acetic acid/sodium acetate of 0.9 and had a moisture content of 0.17%. The extrusion rate of the EVOH through a Koka Flow Tester at at temperature of 220°C did not substantially increased over 10 hours ($V_{10}/V_0 = 0.30$).

Bottles were formed in the same manner as in Example 1 from the EVOH pellets thus obtained. The bottles were filled with orange juice and then subjected to the dropping test. Of the 20 bottles tested, 15 were broken and the breakage ratio was 75%. They broke at the pinch-off part, more specifically the handle part, which fact indicates low adhesiveness between the EVOH composition layer and the adhesive resin layer.

Example 5

A multilayered container having a construction of EVOH/low-density polyethylene/paperboard/low-density polyethylene was formed with the EVOH composition obtained in Example 3 used for the innermost layer, in the following manner. Both sides of a paperboard having a thickness of 500 μm were flame treated, and then a low-density polyethylene having an MI (190°C, 2160 g) of 0.7 g/10 min and a density of 0.92 g/cm³ (hereinafter referred to as LDPE) was extrusion laminated on one side of the paperboard to form an LDPE layer of 38 μm thickness. Next, the LDPE was extrusion laminated on the other side of the paperboard to form an LDPE layer of 16 μm thickness. The surface of the LDPE layer of 16 μm thickness was corona discharged, followed by extrusion lamination thereon of the EVOH composition obtained in Example 3 thereon to form the EVOH composition layer of 20 μm thickness. The multilayered structure thus formed was cut, folded and heatsealed at the closing part to give a rectangular parallelepiped container of 1-liter capacity. The container thus formed was filled with 0.9 liter of 100% lemon juice, and the package was stored at 5°C for 6 weeks. After the storage, the lemon juice contained was tested for the content of d-limonene and by the organoleptic test for flavor and taste by 5 panelists. The results are shown in Table 2. The content of d-limonene was determined, in the same manner as in Example 1, by head-space gas chromatography. The ratings for flavor and taste were, based on those of fresh lemon juice, as follows:

A: same as the flavor or taste of fresh lemon juice

B: a little different from the flavor or taste of fresh lemon juice but not unpleasant.

C: different from the flavor or taste of fresh lemon juice and unpleasant

Example 6

Procedures similar to those described in Example 1 were followed to prepare an EVOH composition containing acetic acid, potassium acetate and sodium dihydrogenphosphate and an EVOH having an ethylene content of 70 mol%, a saponification degree of 98.1 mol%, an MI (210°C, 2160 g) of 80 g/10 min and a melting point of 125°C. The EVOH composition obtained contained 80 ppm of potassium acetate as converted to potassium, 130 ppm of acetic acid, 120 ppm of sodium dihydrogenphosphate as converted to phosphate ion, 6 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH composition showed a content ratio of acetic acid/potassium acetate of 0.65, and had a moisture content of 0.05%. The extrusion rate of the EVOH through a Koka Flow Tester at a temperature of 150°C did not substantially increase over 10 hours ($V_{10}/V_0 = 0.71$).

The EVOH pellets thus obtained were formed into the same multilayered container as that described in Example 5 in the same manner as in Example 5. The container thus formed was tested for storing capability for lemon juice. The results are also shown in Table 2.

Comparative Example 9

Example 5 was repeated to form the same multilayered container except that a commercial EVOH composition was used instead of the EVOH composition used in Example 5. The commercial EVOH contained 450 ppm of sodium acetate as converted to sodium, 10 ppm of acetic acid, 0 ppm of phosphate ion, 6 ppm of calcium and not more than 1 ppm of metals belonging to group II of the periodic table except calcium. The EVOH showed a content ratio of acetic acid/sodium acetate of 0.065, and had a moisture content of 0.15%, an ethylene content of 40 mol%, a saponification degree of 99.3 mol% and an MI (210°C, 2160 g) of 10 g/10 min. The container formed was tested for storing capability for lemon juice. The results are also shown in Table 2. A strong burning odor was noticed with the container.

Comparative Example 10

Example 5 was repeated to form the same multilayered container except that a commercial EVOH composition having an ethylene content of 88.8 mol%, a saponification degree of 97.3 mol%, and an MI (210°C, 2160 g) of 18 g/10 min was used instead of the EVOH composition used in Example 5. The container formed was tested for storing capability for lemon juice. The results are also shown in Table 2.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

Table 1

	d-Limonene	Organoleptic test	
	(volume %)	flavor	taste
Example 1	0.58	A	A
Example 2	0.59	A	A
Example 3	0.56	A	A
Example 4	0.55	A	A
Comp. Ex. 1	0.18	C	C
Comp. Ex. 2	0.58	C	C
Comp. Ex. 3	0.56	B	C
Comp. Ex. 4	0.58	C	B
Comp. Ex. 5	0.57	C	C
Note 1: The content of d-limonene in the fresh orange juice was 0.61 vol%.			
Note 2: The ratings for flavor and taste were, based on those of fresh juice, as follows:			
A: same as the flavor or taste of fresh orange juice			
B: a little different from the flavor or taste of fresh orange juice but not unpleasant.			
C: different from the flavor or taste of fresh orange juice and unpleasant.			

Table 2

	d-Limonene	Organoleptic test	
	(volume %)	flavor	taste
Example 5	0.83	A	A
Example 6	0.78	A	A
Comp. Ex. 9	0.79	B	C
Comp. Ex. 10	0.35	C	C
Note 1: The content of d-limonene in the fresh lemon juice was 0.85 vol%.			
Note 2: The ratings for flavor and taste were, based on those of fresh lemon juice, as follows:			
A: same as the flavor or taste of fresh lemon juice			
B: a little different from the flavor or taste of fresh lemon juice but not unpleasant.			
C: different from the flavor or taste of fresh lemon juice and unpleasant.			

Claims

1. A composition comprising a saponified product of an ethylene-vinyl acetate copolymer having an ethylene content of 20 to 80 mol% and a saponification degree of the vinyl acetate component of at least 95 mol%, said composition containing 20 to 200 ppm as converted to alkali metal of an alkali metal acetate, not more than 10 ppm of metals belonging to the group II of the periodic table, 30 to 250 ppm of acetic acid, and 5 to 500 ppm as converted to phosphate ion of phosphoric acid or an alkali metal hydrogenphosphate, and having a content ratio of acetic acid/alkali metal acetate of from 0.1 to 1 and the flow characteristic that the extrusion rate with a capillary rheometer (Koka Flow Tester) at at least one temperature from 10° to 80°C above the melting point does not increase to an extent that V_{10}/V_0 is more than 1.1, V_0 and V_{10} being the extrusion rate at the beginning and 10 hours after the beginning of heating, respectively.
2. A multilayered container having a layer formed by the use of a composition of Claim 1 as the innermost layer.
3. The multilayered container of Claim 2 comprising at least 2 layers wherein a layer formed by the use of a composition of Claim 1 constitutes the innermost layer and a layer of a thermoplastic resin having a low water absorbability constitutes an outer layer.
4. The multilayered container of Claim 2 comprising at least 3 layers wherein a layer formed by the use of a composition of Claim 1 constitutes the innermost layer and a layer of a thermoplastic resin having a low water absorbability

and a paper layer constitute outer layers.

- 5 5. The multilayered container of Claim 3 wherein said thermoplastic resin having a low water absorbability is at least one of polyethylene, polypropylene, ethylene-propylene copolymers, ethylene-vinyl acetate copolymers, thermoplastic polyesters, polyamides, polystyrene and polycarbonates.
6. The multilayered container of Claim 4 wherein said thermoplastic resin having a low water absorbability is at least one of polyethylene, polypropylene, ethylene-propylene copolymers and ethylene-vinyl acetate copolymers.
- 10 7. A package comprising the multilayered container of Claim 3, said package containing a liquid article or paste article such that the article contacts the layer formed by the use of a composition of Claim 1 of said container.
8. A food package comprising the multilayered container of Claim 3, said package containing a liquid food such that said food contacts the layer formed by the use of a composition of Claim 1 of said container.
- 15 9. The food package of Claim 8 wherein said liquid food is a citrus fruit juice or a refreshing beverage containing a large amount of a citrus fruit juice.

20 Revendications

1. Composition comprenant un produit saponifié d'un copolymère d'éthylène-vinylacétate ayant une teneur en éthylène de 20 à 80 % en mole et un degré de saponification du composant d'acétate de vinyle d'au moins 95 % en mole, la composition contenant 20 à 200 ppm tels que convertis en métal alcalin d'un acétate des métaux alcalins, pas plus de 10 ppm de métaux faisant partie du Groupe II de la Classification Périodique des Eléments, 30 à 250 ppm d'acide acétique et 5 à 500 ppm tels que convertis en ion phosphate de l'acide phosphorique ou d'un phosphate hydrogéné des métaux alcalins, et ayant un rapport de teneur acide acétique/acétate des métaux alcalins allant de 0,1 à 1 et la caractéristique d'écoulement telle que la vitesse d'extrusion à l'aide d'un rhéomètre capillaire (Koka Flow Tester) à au moins une température allant de 10 à 80°C au-dessus du point de fusion n'augmente pas dans des proportions telles que V_{10}/V_0 dépasse 1,1, V_0 et V_{10} étant la vitesse d'extrusion respectivement au début et 10 heures après le début du chauffage.
2. Récipient multicouche ayant une couche formée par l'utilisation d'une composition selon la revendication 1, en tant que couche interne extrême.
- 35 3. Récipient multicouche selon la revendication 2, comprenant au moins 2 couches où une couche formée par l'utilisation d'une composition de la revendication 1 constitue la couche interne extrême et une couche d'une résine thermoplastique ayant une faible capacité d'absorption de l'eau constitue la couche extérieure.
- 40 4. Récipient multicouche selon la revendication 2, comprenant au moins 3 couches où une couche formée par l'utilisation d'une composition de la revendication 1 constitue la couche interne extrême et une couche d'une résine thermoplastique ayant une faible capacité d'absorption de l'eau et une couche de papier constituent les couches extérieures.
- 45 5. Récipient multicouche selon la revendication 3, dans lequel la résine thermoplastique ayant une faible capacité d'absorption de l'eau est au moins une résine parmi les copolymères éthylène-propylène, polypropylène, polyéthylène, les copolymères d'éthylène-vinylacétate, les polyesters thermoplastiques, les polyamides, le polystyrène et les polycarbonates.
- 50 6. Récipient multicouche selon la revendication 4, dans lequel la résine thermoplastique ayant une faible capacité d'absorption de l'eau est au moins une résine parmi les copolymères de polyéthylène, polypropylène, éthylène-propylène et les copolymères d'éthylène-vinylacétate.
- 55 7. Emballage comprenant le récipient multicouche selon la revendication 3, cet emballage contenant un produit liquide ou un produit pâteux de telle sorte que le produit vient en contact avec la couche formée par l'utilisation d'une composition selon la revendication 1 du récipient.
8. Emballage pour aliments comprenant le récipient multicouche selon la revendication 3, cet emballage contenant

un aliment liquide de telle sorte que cet aliment vient en contact avec la couche formée par l'utilisation d'une composition de la revendication 1 du récipient.

- 5 9. Emballage pour aliments selon la revendication 8, dans lequel l'aliment liquide est un jus de fruit d'agrumes ou une boisson rafraîchissante contenant une grande quantité de jus de fruit d'agrumes.

Patentansprüche

- 10 1. Zusammensetzung, welche ein Verseifungsprodukt eines Ethylen-Vinylacetat-Copolymers mit einem Ethylengehalt von 20 bis 80 mol% und einem Verseifungsgrad der Vinylacetateinheit von mindestens 95 mol% umfaßt, wobei die Zusammensetzung 20 bis 200 ppm eines Alkalimetallacetates, berechnet als Alkalimetall, nicht mehr als 10 ppm eines Metalls der II. Gruppe des Periodensystems, 30 bis 250 ppm Essigsäure und 5 bis 500 ppm Phosphorsäure oder eines Alkalimetallhydrogenphosphates, berechnet als Phosphation, enthält, ein Verhältnis der Gehalte an Essigsäure/Alkalimetallacetat von 0.1 bis 1 aufweist und ein Fließverhalten zeigt, bei dem die Extrusionsgeschwindigkeit in einem Kapillarrheometer (Koka Flow Tester) bei einer Temperatur von mindestens 10° bis 80°C oberhalb des Schmelzpunktes nicht in einem Ausmaß steigt, bei dem V_{10}/V_0 größer als 1.1 ist, wobei V_0 und V_{10} die Extrusionsgeschwindigkeiten zu Beginn beziehungsweise 10 Stunden nach Beginn der Erwärmung sind.
- 15 2. Mehrschichtiger Behälter mit einer unter Verwendung einer Zusammensetzung gemäß Anspruch 1 hergestellten Schicht als innerste Schicht.
3. Mehrschichtiger Behälter gemäß Anspruch 2, welcher mindestens 2 Schichten umfaßt, wobei eine unter Verwendung einer Zusammensetzung gemäß Anspruch 1 hergestellte Schicht die innerste Schicht darstellt und eine Schicht eines thermoplastischen Harzes mit geringer Wasseraufnahmefähigkeit eine äußere Schicht darstellt.
- 25 4. Mehrschichtiger Behälter gemäß Anspruch 2, welcher mindestens 3 Schichten umfaßt, wobei eine unter Verwendung einer Zusammensetzung gemäß Anspruch 1 hergestellte Schicht die innerste Schicht darstellt und eine Schicht eines thermoplastischen Harzes mit geringer Wasseraufnahmefähigkeit und eine Papierschicht äußere Schichten darstellen.
- 30 5. Mehrschichtiger Behälter gemäß Anspruch 3, wobei das thermoplastische Harz mit geringer Wasseraufnahmefähigkeit mindestens eins aus der Gruppe ist, die aus Polyethylen, Polypropylen, Ethylen-Propylen-Copolymeren, Ethylen-Vinylacetat-Copolymeren, thermoplastischen Polyestern, Polyamiden, Polystyrol und Polycarbonaten besteht.
- 35 6. Mehrschichtiger Behälter gemäß Anspruch 4, wobei das thermoplastische Harz mit geringer Wasseraufnahmefähigkeit mindestens eins aus der Gruppe ist, die aus Polyethylen, Polypropylen, Ethylen-Propylen-Copolymeren, Ethylen-Vinylacetat-Copolymeren besteht.
- 40 7. Verpackung, die den mehrschichtigen Behälter gemäß Anspruch 3 umfaßt, wobei die Verpackung einen flüssigen Artikel oder eine Paste so beinhaltet, daß der Artikel mit der unter Verwendung einer Zusammensetzung gemäß Anspruch 1 hergestellten Schicht des Behälters in Berührung kommt.
- 45 8. Nahrungsmittelverpackung, welche den mehrschichtigen Behälter gemäß Anspruch 3 umfaßt, wobei die Nahrungsmittelverpackung ein flüssiges Nahrungsmittel so beinhaltet, daß das Nahrungsmittel mit der unter Verwendung einer Zusammensetzung gemäß Anspruch 1 hergestellten Schicht des Behälters in Berührung kommt.
- 50 9. Nahrungsmittelverpackung gemäß Anspruch 8, wobei das flüssige Nahrungsmittel ein Zitrusfruchtsaft oder ein Erfrischungsgetränk, welches eine große Menge eines Zitrusfruchtsaftes enthält, ist.

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